CHEMISTRY OF DEFENSIVE SECRETIONS OF OZAENINE AND PAUSSINE BOMBARDIER BEETLES (COLEOPTERA: CARABIDAE)[1]

Bradie Roach, Kenneth R. Dodge, Daniel J. Aneshansley, David Wiemer[2], J. Meinwald, and T. Eisner

Section of Neurobiology and Behavior and Department of Chemistry, Cornell University, Ithaca, NY 14853

Abstract

1,4-Benzoquinones and a hydrocarbon are identified from the defensive secretions of six ozaenine and one paussine species.

In previous papers from our laboratories we dealt with the chemistry, behavior, and predator-prey relations of bombardier beetles, including species of Brachinini, Metriini, Ozaenini, and Paussini (Aneshansley *et al.* 1969; Eisner 1958; Eisner and Dean 1976; Eisner *et al.* 1977). We now have had occasion to study a number of additional live ozaenines, as well as one paussine previously available to us only in moribund condition. We here report on the chemistry of the defensive secretions of these beetles.

The insects were collected on Barro Colorado Island, Canal Zone, and sent to our Cornell laboratories by mail. They were identified by Dr. Terry L. Erwin of the National Museum of Natural History, Smithsonian Institution, Washington, D.C. Two species, previously undescribed, are herein called *Goniotropis* no. 3 and *Pachyteles* no. 31 and deposited under that designation in Dr. Erwin's Central American series in the National Museum collection. The procedures for maintaining the animals live in the laboratory, for "milking" them of their secretions, and for identifying and quantifying the secretory components, were as previously described (Eisner *et al.* 1977). The one constituent not previously detected in bombardier beetle secretion, 2-ethyl-1,4-benzoquinone, was identified on the basis of direct gas chromatographic and mass spectral comparison with an authentic sample.

Chemical analyses were done of one set of milkings from all beetles, and of a second set of milkings, taken 40 days later, from those beetles that survived over this period of time. The compounds identified, and their relative proportions in the milkings of the individual beetles, are shown in Table 1.

The data clearly support the emergent generalization that 1,4-benzoquinone production is the norm for bombardier beetles. 2-Methyl-1,4-benzoquinone appears to be the dominant quinone in the Ozaenini. This holds for the 6 species reported here, as it did for the 3 species studied previously (Eisner *et al.* 1977). 1,4-Benzoquinone itself and its 2,3-dimethyl derivative are consistently present in lesser concentrations in these beetles. 2-Ethyl-1,4-

---

[1]Report no. 62 in the series *Defense Mechanisms of Arthropods*. Report no. 61 is: J. Meinwald, D. F. Wiemer, T. Eisner, *J. Amer. Chem. Soc.*, in press (1978).

[2]Present address: Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

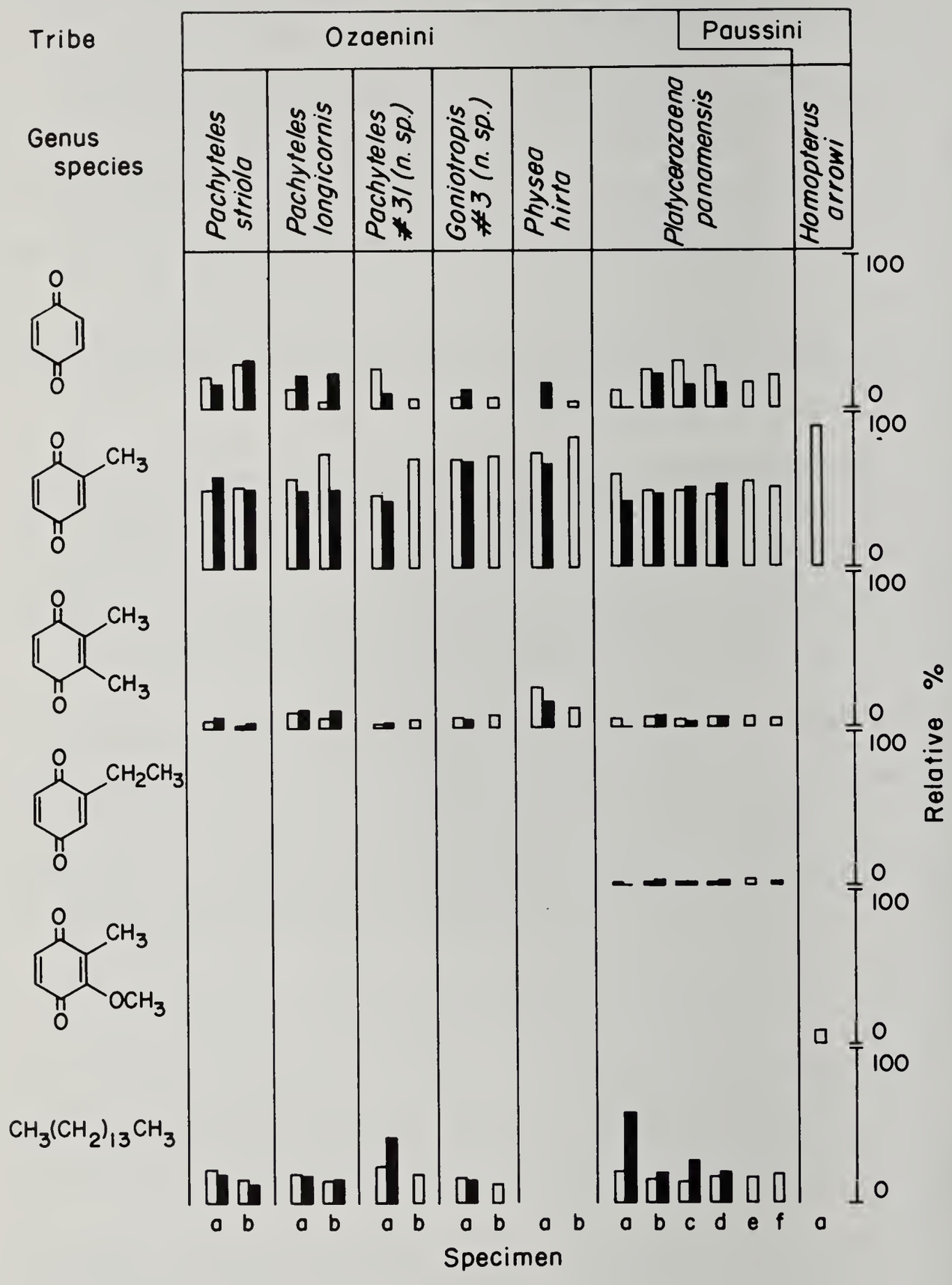

Table 1. Relative percentages of 1,4-benzoquinones and *n*-pentadecane in defensive secretions of individual ozaenine and paussine beetles. Percentages are given by bar heights; white bars = first milkings; black bars = second milkings (not taken in some cases).

benzoquinone, found in low concentrations in *Platycerozaena panamensis* only, has hitherto been found in no other Ozaenini, or for that matter in bombardier beetles of other tribes. Hydrocarbon production, and particularly *n*-pentadecane production, is also commonplace in bombardiers. In fact, *Physea hirta* is the only species of Ozaenini so far known that lacks this compound in its secretion.

We had previously reported (Eisner *et al.* 1977) the paussine *Homopterus arrowi* to produce 2-methyl-1,4-benzoquinone and 2-methyl-3-methoxy-1,4-benzoquinone. However, our identifications were based on secretion generated artificially by mixing the contents of the two chambers of glands excised from a moribund specimen that could no longer be induced to spray on its own (Eisner *et al.* 1977), and some questions remained about the validity of these chemical findings. The data reported here were derived from a sample of secretion discharged in normal fashion by a specimen of *H. arrowi* that reached our Cornell laboratories in vigorous condition. The presence of the two quinones previously identified is now confirmed for this beetle (at virtually the same relative proportions as previously reported), as is the absence of accompanying hydrocarbon.

As is apparent from the table, there is relatively little variability in secretory composition from individual to individual in any species of Ozaenini, or from milking to milking in any given individual. But constancy did not always prevail (note, for example, the quantitative and qualitative differences between first and second milkings of *Physea hirta* specimen a, and *Platycerozaena panamensis* specimen a). Phyletic conclusions derived from chemical studies of bombardier beetles will obviously need to take into account such variability and its potential for occurrence in any species.

Acknowledgements

The beetles were collected by Dr. Robert E. Silberglied and Ms. Anette Aiello. Study supported in part by grants AI-02908 (NIH) and PCM 77-15914 (NSF).

References Cited

Aneshansley, D. J., T. Eisner, J. M. Widom, and B. Widom. 1969. Biochemistry at 100°C: explosive secretory discharge of bombardier beetles (*Brachinus*). Science 165:61-63.

Eisner, T. 1958. The protective role of the spray mechanism of the bombardier beetle, *Brachynus ballistarius* Lec. J. Insect Physiol. 2:215-220.

Eisner, T., and J. Dean. 1976. Ploy and counterploy in predator-prey interactions: orb-weaving spiders versus bombardier beetles. Proc. Nat. Acad. Sci. USA 73:1365-1367.

Eisner, T., T. H. Jones, D. J. Aneshansley, W. R. Tschinkel, R. E. Silberglied, and J. Meinwald. 1977. Chemistry of defensive secretions of bombardier beetles (Brachinini, Metriini, Ozaenini, Paussini). J. Insect Physiol. 23:1383-1386.